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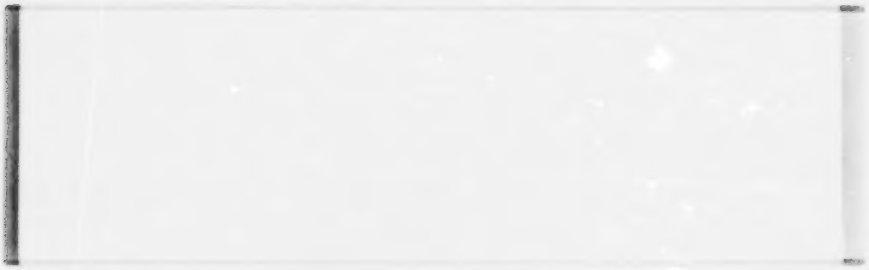

Canada

SULPHIDE DUST EXPLOSIONS: MEASUREMENT OF SO_2 BY INFRARED SPECTROSCOPY

K.J. Mintz

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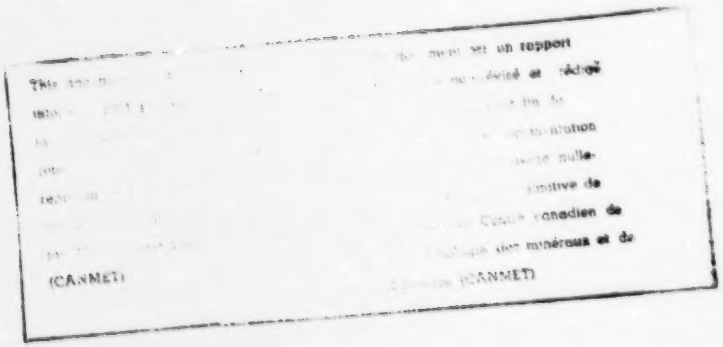

SULPHIDE DUST EXPLOSIONS: MEASUREMENT OF SO_2 BY INFRARED SPECTROSCOPY

by

K.J. Mintz*

ABSTRACT

Toxic sulphur dioxide gas is the major problem arising from sulphide dust explosions that occur frequently in Canadian metal mines. A method to measure the quantity of SO_2 produced from laboratory explosion testing has been developed using infrared spectroscopy. Fourteen calibration curves are presented. The potential errors in this method are discussed and a detailed procedure provided.

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KEYWORDS: dust explosions, sulphide ores, sulphur dioxide, infrared spectroscopy

EXPLOSIONS DE POUSSIÈRES SULFURÉES: DOSAGE DU SO_2 PAR SPECTROSCOPIE INFRAROUGE

par

K.J. Mintz*

RÉSUMÉ

Le dioxyde de soufre, qui est un gaz toxique, constitue le principal problème des explosions de poussières sulfurées qui se produisent fréquemment dans les mines de métaux au Canada. On a mis au point une méthode, faisant appel à la spectroscopie infrarouge, qui permet de doser le SO_2 produit au cours d'essais d'explosion en laboratoire. On présente 14 courbes d'étalonnage. On examine les erreurs possibles dans cette méthode et on donne un mode opératoire détaillé.

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MOTS CLÉS: explosions de poussières, minerais sulfurés, dioxyde de soufre, spectroscopie infrarouge

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INTRODUCTION

During the past several years, sulphide ore dust explosions in Canadian metal mines have become recognized as a significant problem affecting safety and productivity. An industry/government/academic research group was set up in in 1987 following the first conference held on this subject in Manitouwadge in 1986 (1). One session of the 1988 Annual General Meeting of the Canadian Institute of Mining was also devoted to this subject (2).

The major problem arising from sulphide dust explosions usually occurs, not from the effects of the blast itself, but from the large amounts of toxic sulphur dioxide gas produced. CANMET has awarded a contract for construction of equipment for measuring SO_2 in mines during blasting in sulphide-rich ores (3).

Laboratory studies have been carried out in this laboratory on sulphide ores using the Hartmann and the 20-L dust explosion vessels to measure the explosion pressure and the maximum rate of pressure rise (4). This has provided information on the relative explosibility of various ores (5,6). Since SO_2 production is the major problem, it is also necessary to quantify the SO_2 produced in laboratory studies. In the present study, a method was established which enables the rapid and easy determination of SO_2.

SO_2 is an acid gas, therefore, the most direct method of analysis would be an electrochemical one, based on dissolving the SO_2 in water and titrating against a base. This method assumes that no other acid gas is produced. Infrared spectroscopy was chosen instead because it is more specific and can be applied to detect and measure other products of

combustion. Its disadvantage is that it requires considerably more work initially to calibrate it for meaningful quantitative measurements.

APPARATUS

The Miran-80 Computing Infrared Analyzer, with a 20-meter gas cell, was obtained on loan from Noranda Research for this project. Unlike many infrared spectrophotometers, it was designed specifically for quantitative measurements. Its chief disadvantage is that it is a single-beam instrument, which means that the baseline is not flat, instead, it depends on the black-body radiation of the source. Its main advantage is that it provides a digital output of the absorbance at up to 18 user-selectable wavelengths. It also provides an analogue output for generating a spectrum. An Omega model 555 chart recorder was used for recording the analogue spectra.

The 20-meter gas cell is adjustable in path length in 1.5 m increments from 0.75 m to 21.75 m. The longer path lengths are primarily for detecting trace quantities of toxic gases, for example, for compliance with regulated TLV's. Preliminary experiments indicated that substantial quantities of SO_2 were produced; hence, the shortest path length sufficed. In addition, it was possible to use the smallest slit width (0.5 mm) for maximum resolution.

A stainless-steel tube was connected from the 20-meter cell to the 20-L explosion vessel through a plug valve. After the gases have been allowed to cool from an explosion test, this valve can be opened to allow the combustion gases to flow into the previously-evacuated line and 20-m cell, for measurement by the infrared spectrophotometer. The volume of the tubing is 0.8 L, that of the 20-m cell, 5.6 L. Hence, the SO_2 concentration must

be multiplied by 20/(20 + 5.6 + 0.8) = 0.758, to obtain the true concentration in the 20-L vessel.

For calibrations, anhydrous grade SO_2 (Matheson), containing 99.98% SO_2, was used at high concentrations and a 1.42% mixture of SO_2 in air (Matheson) was used at low concentrations. In both cases, the whole system was pumped out thoroughly, then the required quantity of gas added. The concentration of SO_2 was calculated from the pressure measured by the CEC 1000 strain-gauge pressure transducer. Dry air was added to bring the total pressure to 101 kPa absolute.

RESULTS AND DISCUSSION

Infrared Spectrum

The analogue spectrum of Matheson dry air as generated by the Miran-80 is shown in Fig. 1. The ordinate scale, % transmittance, is the fraction of radiation that is not absorbed. Two filter changes make the regions 4.3 - 4.6 μm and 7.8 - 8.2 μm inaccessible. Note that the abscissa is linear in wavelength for each of the three filters, but the scale factor changes when the filter changes. As mentioned above, the sloping baseline is due to the use of a single-beam instrument. The water and the carbon dioxide absorption bands are quite significant and can cause problems if the absorption band of interest is at the same wavelength. Laboratory air produced a very similar spectrum except that the CO_2 absorption band was only about two-thirds as large.

SO_2 has its main absorption band at about 7.3μm (7). Unfortunately, this peak occurs in the midst of the water band and thus is subject to interference. Therefore, a weaker absorption band at 9μm, in a

spectral region free from interference by water and CO_2, was used.

Absorbance Measurements

The Beer-Lambert Law relates the quantity of light absorbed to the concentration by the expression (8):

$$A = abC$$

where A = absorbance

a = absorptivity

b = path length

C = concentration.

The absorptivity is a constant dependent only upon the wavelength and the nature of the absorbing species. The absorbance is defined in terms of the transmittance, T, as:

$$A = \log_{10}(1/T)$$

Absorbance values are generated directly by the Miran-80 for up to 17 sample wavelengths plus a reference wavelength. The instrument was zero'd at these wavelengths by filling the cell with dry air at 101 kPa absolute. It was found that the drift was small, so that this procedure had to be carried out only once or twice a day. The reference wavelength must be selected in a region where the species of interest do not absorb. An inspection of the spectra of dry air and SO_2 led to a choice of 3.8 μm. To confuse the issue somewhat, the value actually printed by the Miran-80 is the absorbance at the wavelength minus the absorbance at the reference wavelength. Ideally, the latter is zero, if the choice of wavelength were good. According to the instruction manual, "band-ratioing to a reference wavelength greatly improves the stability and drift of the instrument". It was found, however, that it did not, rather that the uncorrected absorbance

values were more stable. The only use of the reference wavelength was as an indicator of drift or instability.

Ideally, a plot of absorbance versus concentration should be linear, which would make it easy to calculate the concentration from the measured absorbance. Unfortunately, there are often deviations from the Beer-Lambert Law, which necessitates determination of the calibration curves over the range of concentrations required.

Effect of Pressure

Unlike the other tests, this set of tests are referenced to vacuum, not atmospheric air pressure. 5.7 kPa of SO_2 (equivalent to 150 mg/L) was added to the gas cell, which produced the lowest curve in Fig. 2. Additional quantities of dry air were added, producing the other curves shown in Fig. 2. Notice that the dependence on pressure is greatest at the lowest pressures; the difference between 81 kPa and 100 kPa is almost negligible. The pressure dependences at the different wavelengths are almost identical; the only real change in the shape of the absorption band was the elimination of the two separate peaks. This change in shape is most likely due to pressure-broadening (caused by collisions between the absorbing molecules, which broadens the distribution of energy) .

These results indicate that it is unnecessary to be too concerned about adding extra dry air to the cell to bring the pressure up to exactly atmospheric, provided the total pressure is above about 80 kPa absolute. This reduces the effort in analyzing the SO_2 after an explosion test.

Effect of Concentration

Various pressures of SO_2 were added to the previously-evacuated

gas cell, and dry air was added to bring the pressure up to atmospheric. Figure 3 shows that the peak shape changes slightly, mainly due to the elimination of the two separate peaks. Although superficially similar to the set of curves in the previous section, this change cannot be attributed to pressure-broadening. The cause may be instrumental: the resolution of the instrument is rather poor (about 0.2 μm), plus, possibly, lack of linearity of the instrument at absorbance higher than 0.5.

Figures 4 - 17 show the calibration curves for 14 different wavelengths of the 9 μm band. Every one exhibits distinct curvature, with the ones nearer the centre of the band having the greatest curvature. For low concentrations, a linear fit can be made, as shown in Table 1, for use in calculating the concentration. If a precision of 5% on the concentration is required, it is necessary to use wavelengths where the absorbance is at least 0.04. On the other hand, some of the calibration plots curve over so much at the higher concentrations that the absorbance cannot predict a sufficiently precise concentration. The upper limits within which the calibration curves can be used effectively are given in Table 2.

Although the concentration of SO_2 can be calculated from the absorbance at only one wavelength, it is best to use several in order to eliminate the possibility of gross errors. If the values calculated from the different wavelengths differ significantly, then it indicates that there may be some problem such as the presence of some absorbing species in those wavelengths. The amount of extra work is minimal.

An example of results and calculation for a pyrite dust explosion is shown in Table 3. Applying equal weight to all the data, the mean calculated concentration is 123 $\pm$ 4 mg/L. Hence, the total amount of SO_2 produced was 0.123 g/L X 26.4 L = 3.25 g. The scatter of data is reasonable; the

precision of the mean is within the 5% desired.

Source of Errors

Residual SO_2 adsorbed on the walls of the gas cell (which are Teflon lined) may cause errors unless the cell is evacuated for at least 15 minutes after the previous test, longer if the quantity of SO_2 to be measured is very small. Flushing the cell with dry air may be useful. Recording the absorbances is a useful check.

The instrument prints out the absorbance to 4 decimal points, which may lead to overestimating the accuracy of the measurement. In fact, according to the manufacturer's specifications, the noise level of the spectrophotometer itself (apart from that due to the cell) is about .001 absorbance units in the range used. It is reasonable to assume that the limiting accuracy of the instrument as a whole would be at least double that number.

The Miran-80 with the 20-m cell is designed specifically for quantitative measurement of trace gases, but can be made to work for higher concentrations. Its rather limited resolution may cause some difficulties in measuring mixtures of gases that have absorption bands close to one another.

CONCLUSIONS

The Miran-80 infrared spectrophotometer and, no doubt, other spectrophotometers, can be used to accurately measure the quantity of sulphur dioxide produced by explosion tests in the 20-L vessel. This will enable mass balance to be carried out on the reaction and also correlations to be made with the explosion pressure and other parameters of the system.

Hydrogen sulphide is also reported to be produced sometimes by sulphide ore dust explosions, particularly in the presence of water. A study, similar to this one, should be carried out to enable the measurement of hydrogen sulphide, which may pose a greater hazard because of olfactory fatigue.

If synthetic air, composed of oxygen and nitrogen only, is used for explosion tests of carbonaceous dusts, the carbon dioxide and carbon monoxide produced may provide interesting information on the reactions involved. These species can also be measured quantitatively by infrared spectrophotometry.

ACKNOWLEDGEMENTS

The author is grateful for the loan of the Miran-80 spectrophotometer from Noranda Research Centre.

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Table 1. Linear fit for absorbance of the 9 μm SO_2 absorption band.

Wavelength (μm)	slope (conc./A)	range of validity conc.	A
8.4	1450 ± 30	120	.07
8.45	1100 ± 30	160	.13
8.5	772 ± 15	160	.20
8.55	555 ± 13	160	.26
8.6	398 ± 8	160	.38
8.7	202 ± 2	50	.24
8.8	126 ± 2	30	.30
8.9	105 ± 2	30	.25
9.0	121 ± 2	30	.28
9.1	111 ± 3	30	.35
9.2	143 ± 1	40	.35
9.3	129 ± 2	50	.20

Note: Concentration is in units of mg/L; the uncertainty is the standard deviation of the slope .

Table 2. Range of validity using graphical fit.

Wavelength (μm)	range of validity conc.	A
8.4	450	.20
8.45	450	.30
8.5	450	.45
8.55	450	.60
8.6	465	.75
8.7	300	.80
8.8	200	.80
8.9	160	.85
9.0	200	.85
9.1	160	.85
9.2	170	.80
9.3	240	.75

Table 3. Example calculation of SO_2 concentration.

wavelength (μm)	absorbance	concentration (mg/L)	
		linear fit	graphical
8.5	.1672	129	--
8.55	.2282	127	--
8.6	.3155	126	--
8.7	.5054	n.v.	120
8.8	.6905	n.v.	126
8.9	.7670	n.v.	118
9.0	.7321	n.v.	122
9.1	.7881	n.v.	122
9.2	.6702	n.v.	118
9.3	.4637	n.v.	117

Note: n.v. means not valid.

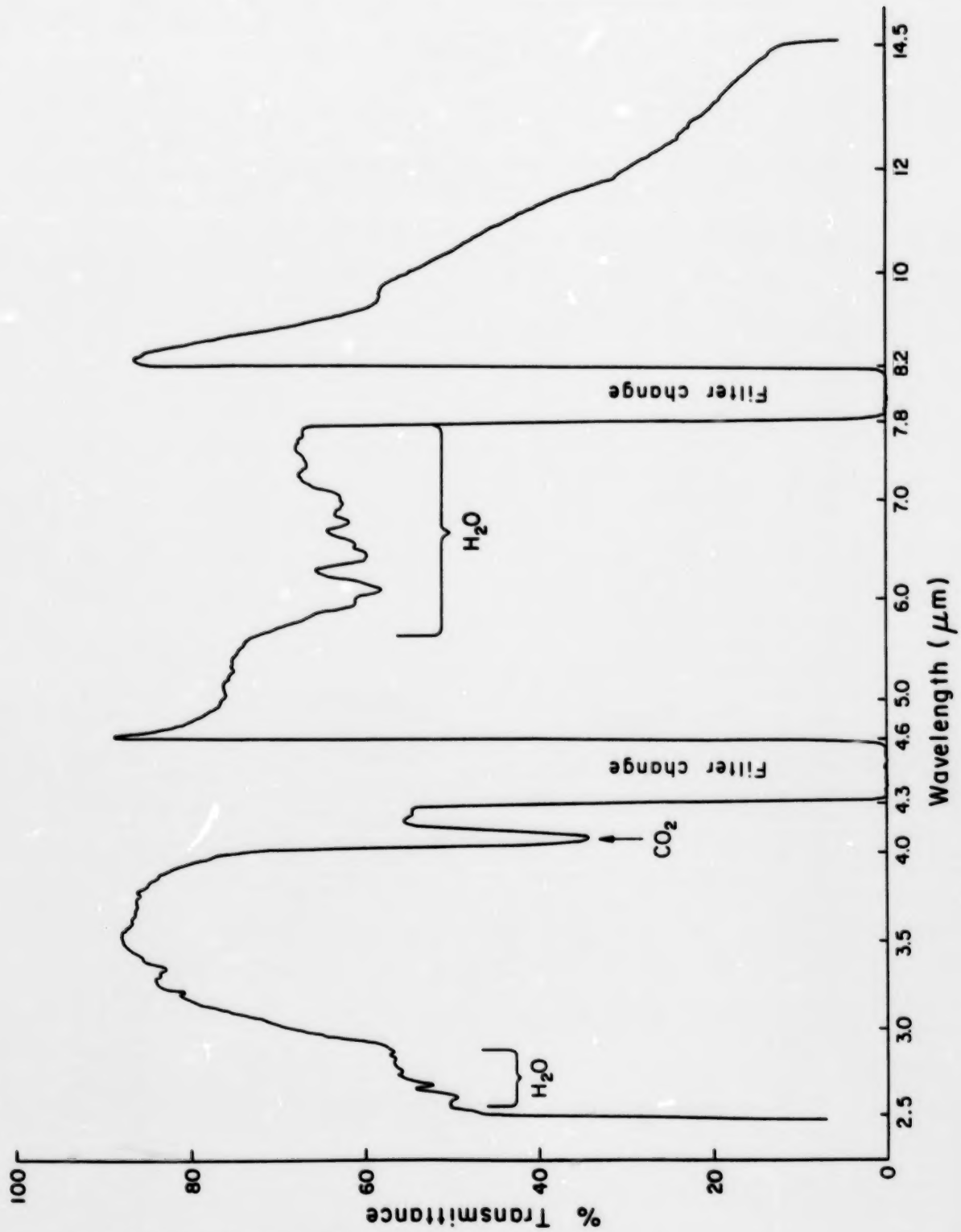

Fig. 1. Infrared spectrum of Matheson dry air

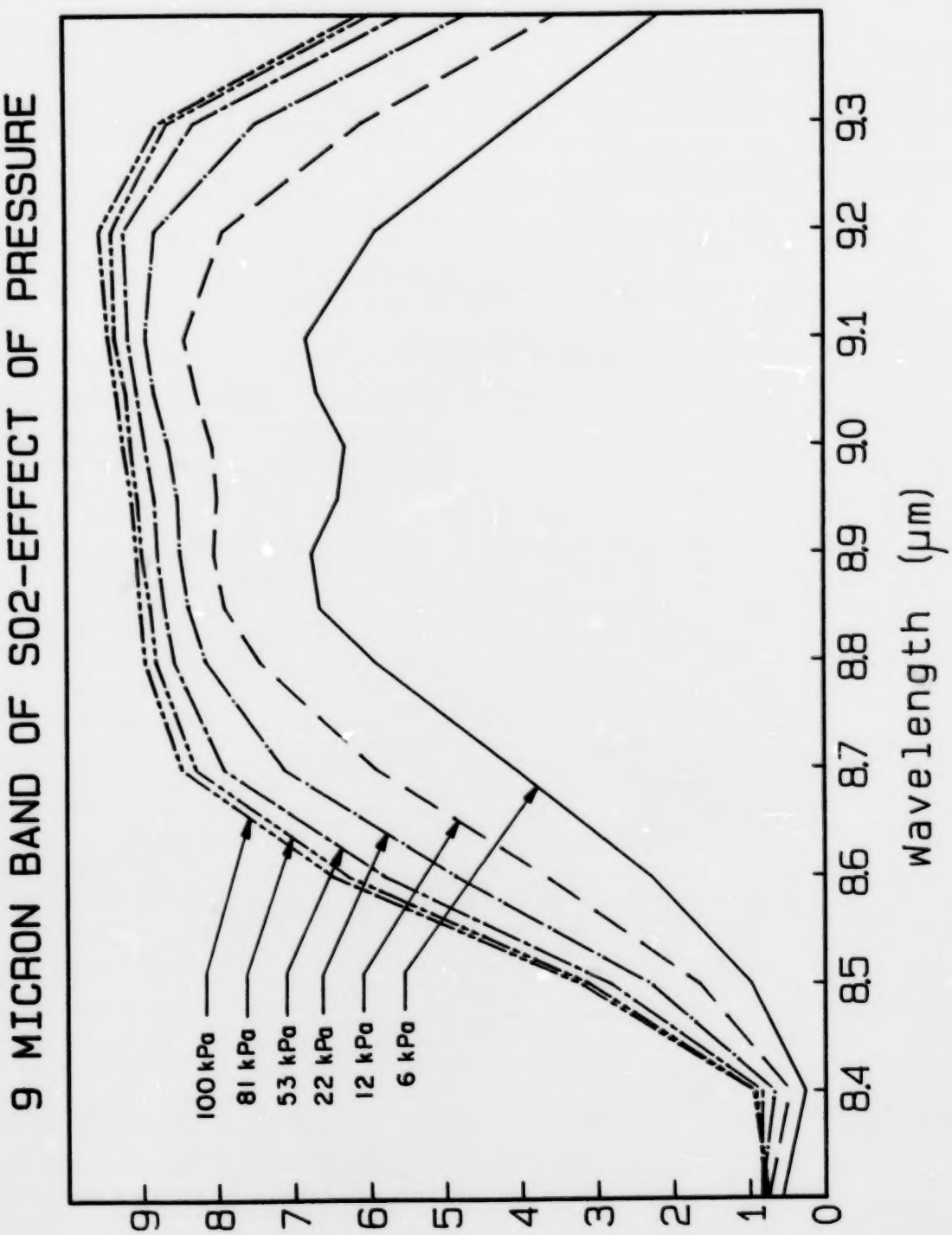
9 MICRON BAND OF SO2-EFFECT OF PRESSURE
100 kPa
81 kPa
53 kPa
22 kPa
12 kPa
6 kPa
Absorbance X 10
0
1
2
3
4
5
6
7
8
9
8.4
8.5
8.6
8.7
8.8
8.9
9.0
9.1
9.2
9.3
Wavelength (μm)

Fig. 2.

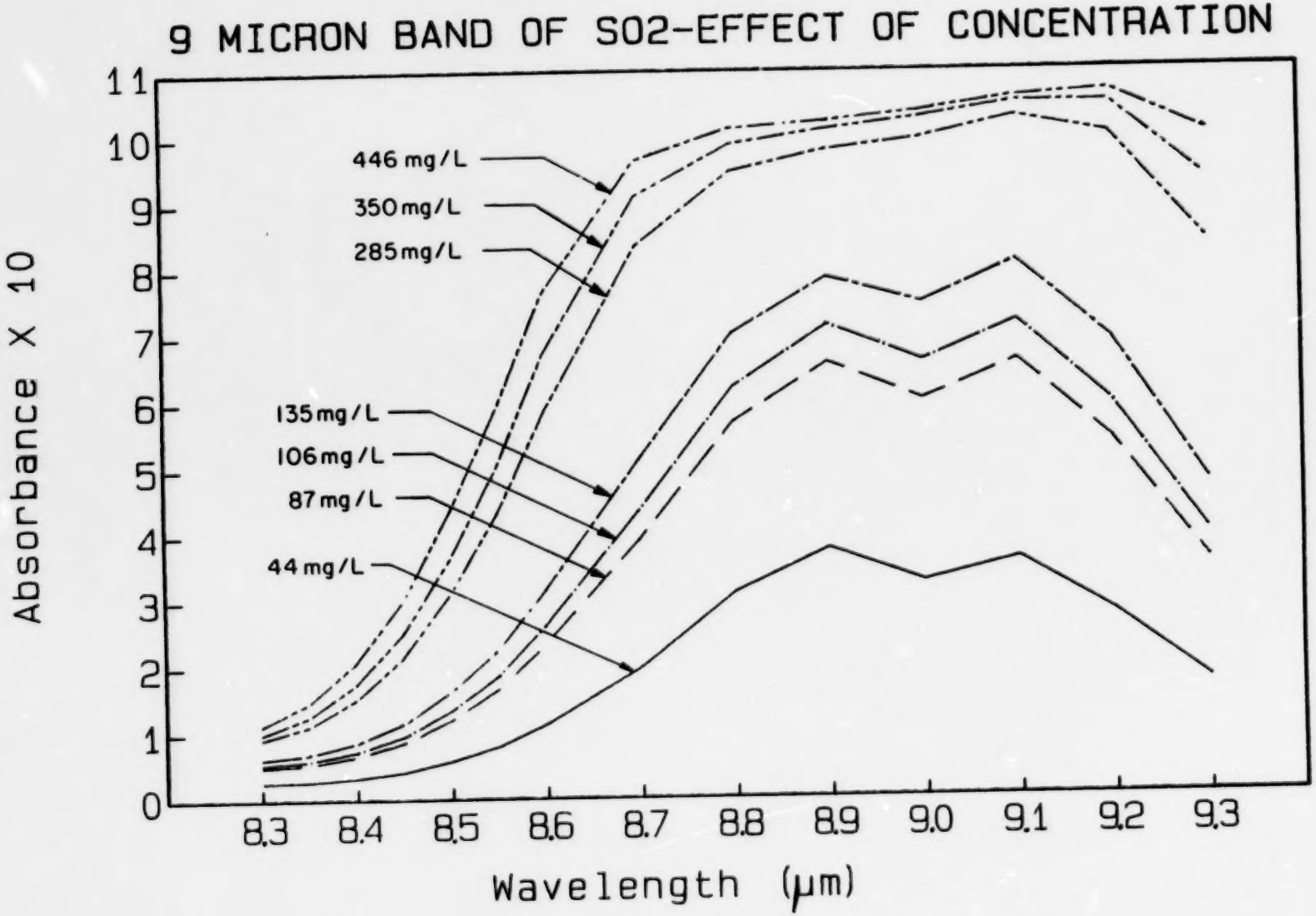
9 MICRON BAND OF SO2-EFFECT OF CONCENTRATION
Absorbance X 10
Wavelength (μm)
446 mg/L
350 mg/L
285 mg/L
135 mg/L
106 mg/L
87 mg/L
44 mg/L
0
1
2
3
4
5
6
7
8
9
10
11
8.3
8.4
8.5
8.6
8.7
8.8
8.9
9.0
9.1
9.2
9.3

Fig. 3

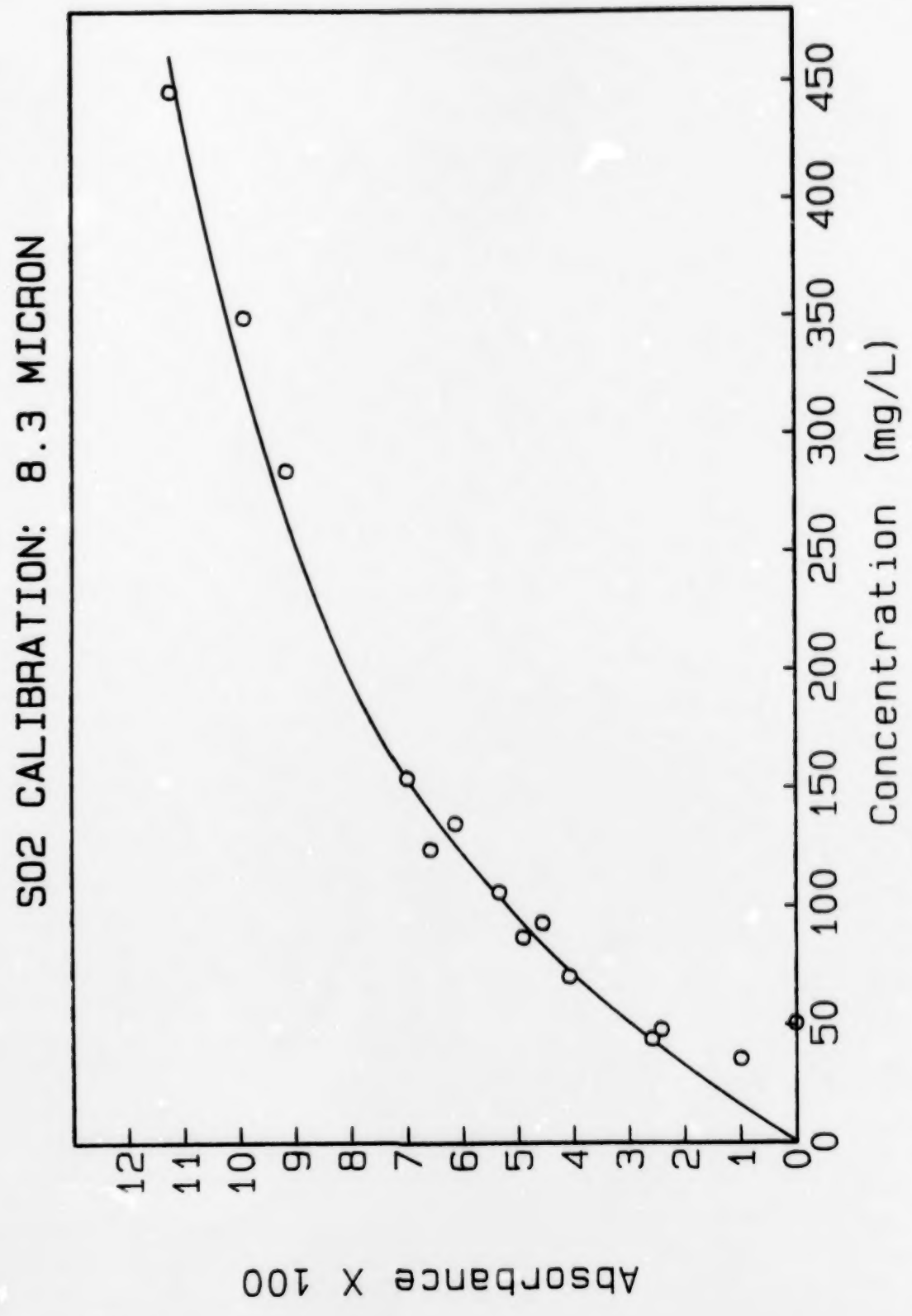
SO2 CALIBRATION: 8.3 MICRON
Absorbance X 100
Concentration (mg/L)
0
1
2
3
4
5
6
7
8
9
10
11
12
0
50
100
150
200
250
300
350
400
450

Fig. 4

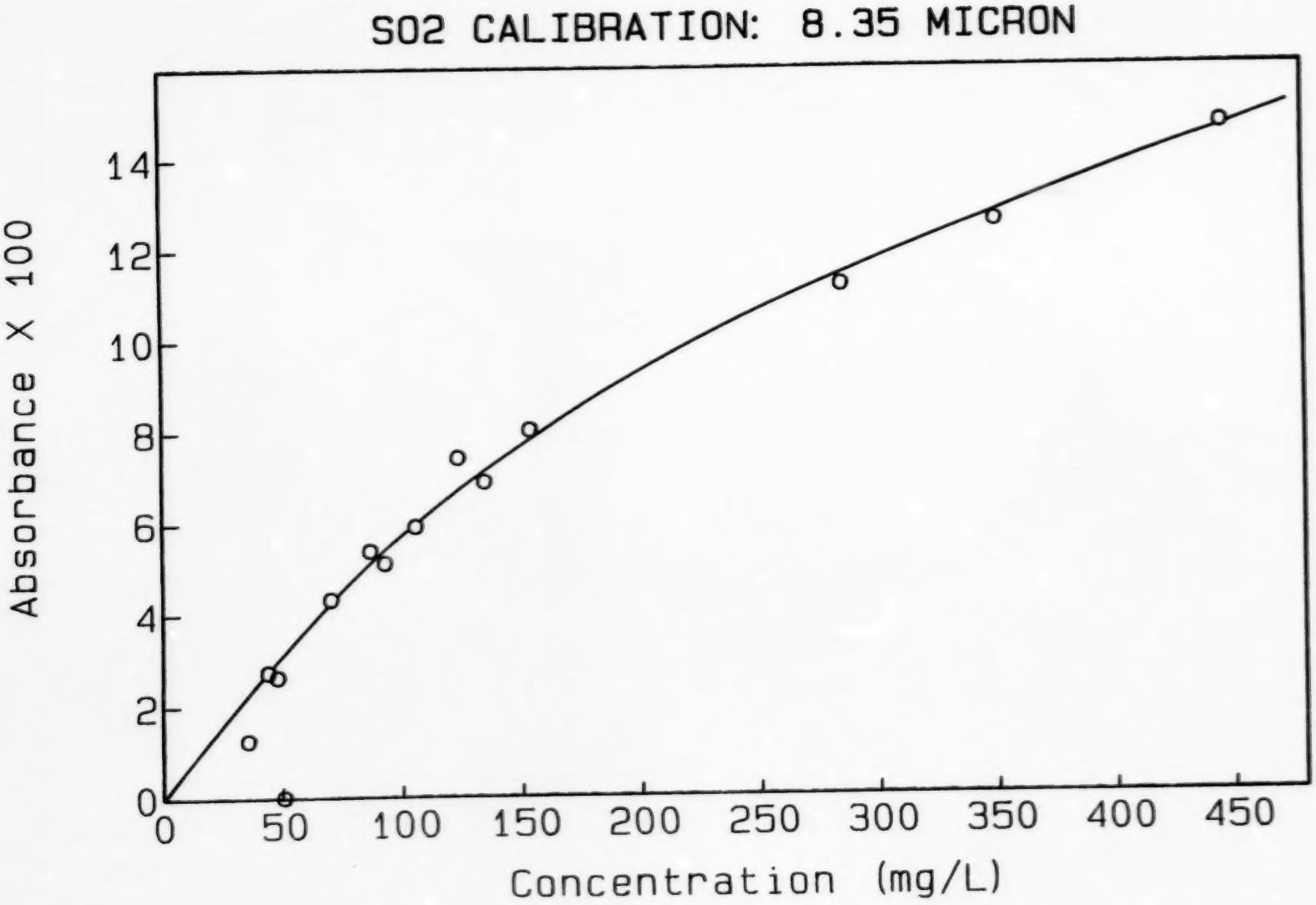
SO2 CALIBRATION: 8.35 MICRON
Absorbance X 100
0
2
4
6
8
10
12
14
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)

Fig. 5

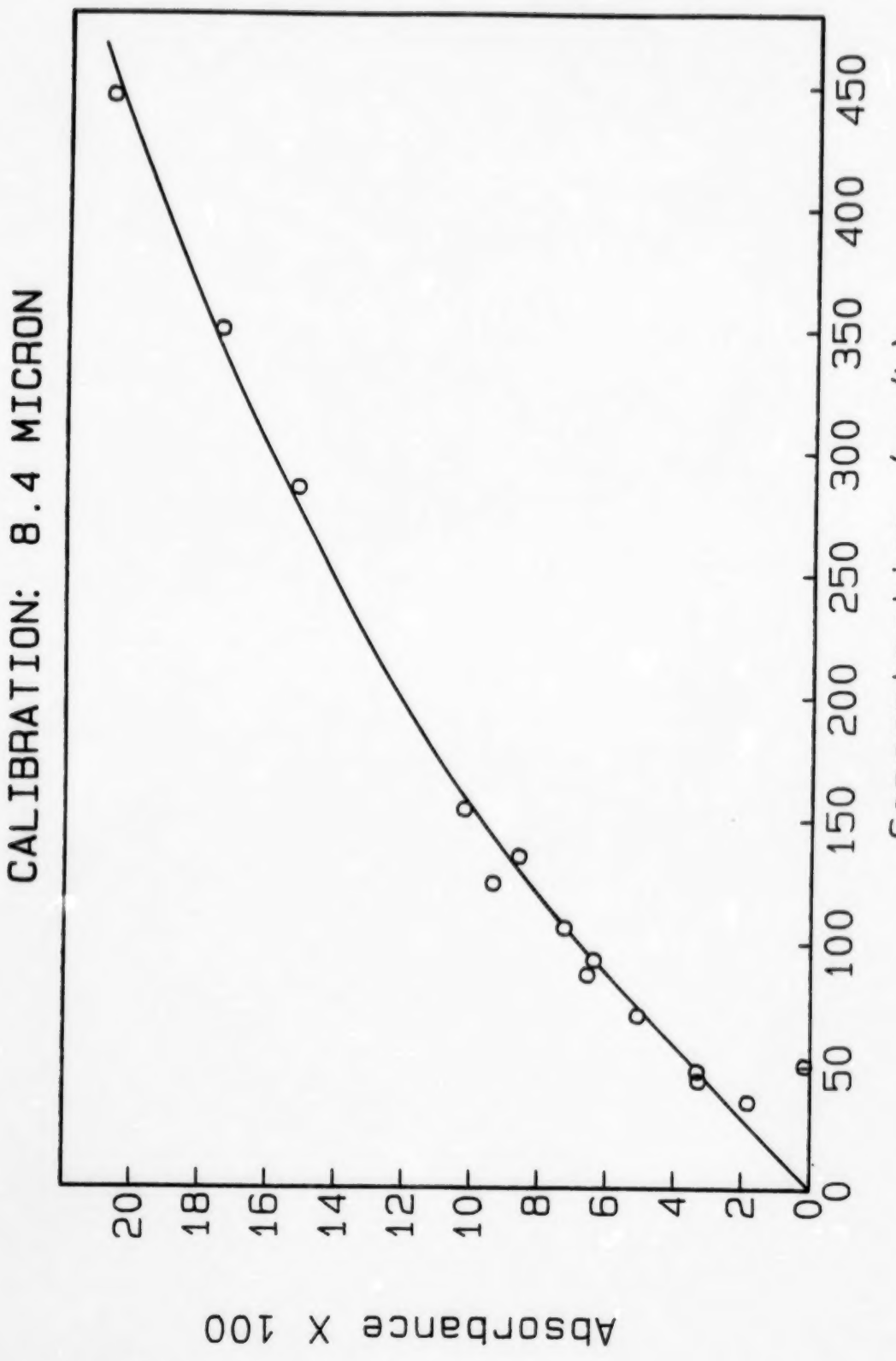
CALIBRATION: 8.4 MICRON
Absorbance X 100
20
18
16
14
12
10
8
6
4
2
0
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)

Fig.6

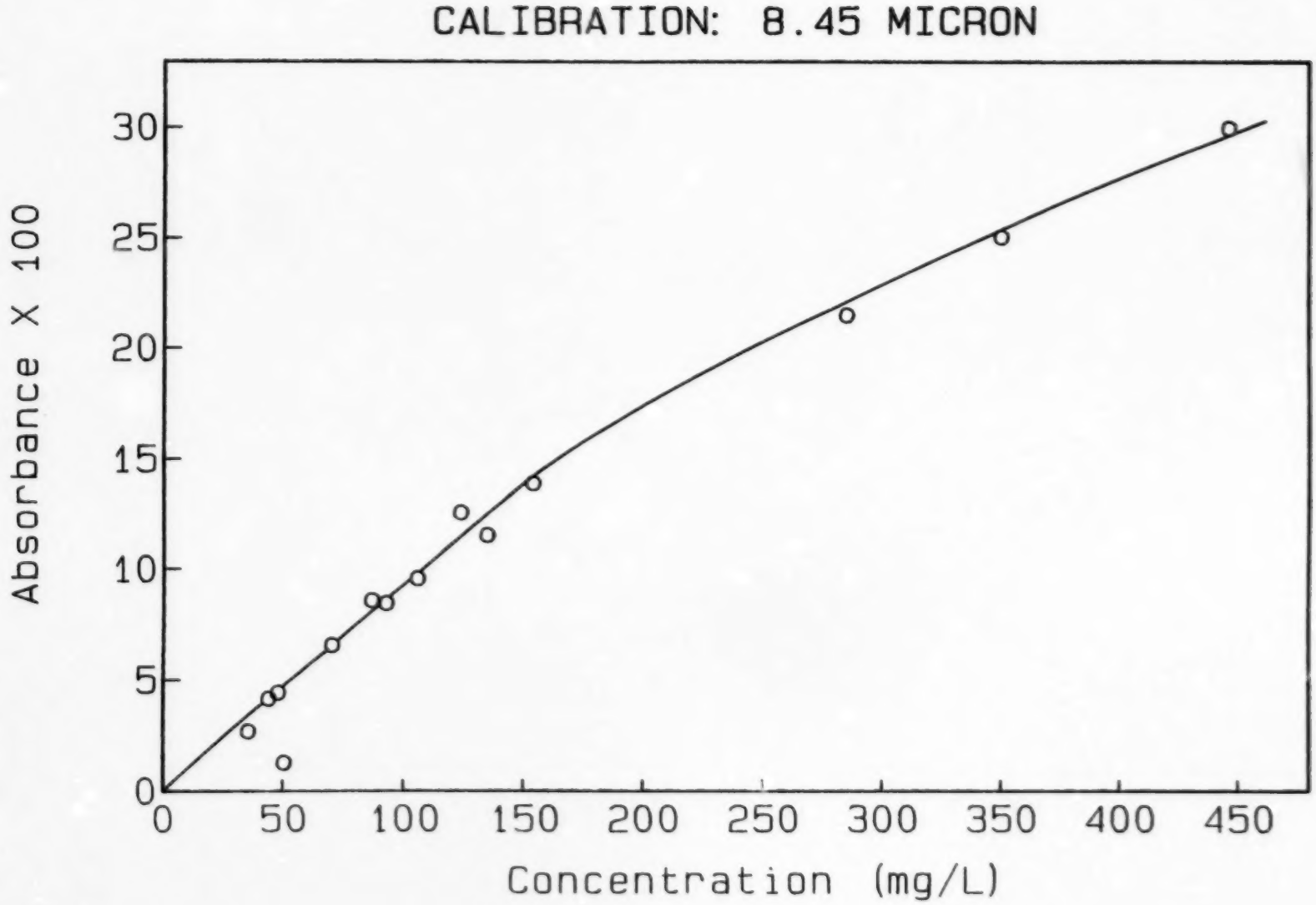
CALIBRATION: 8.45 MICRON
Absorbance X 100
0
5
10
15
20
25
30
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)

Fig. 7

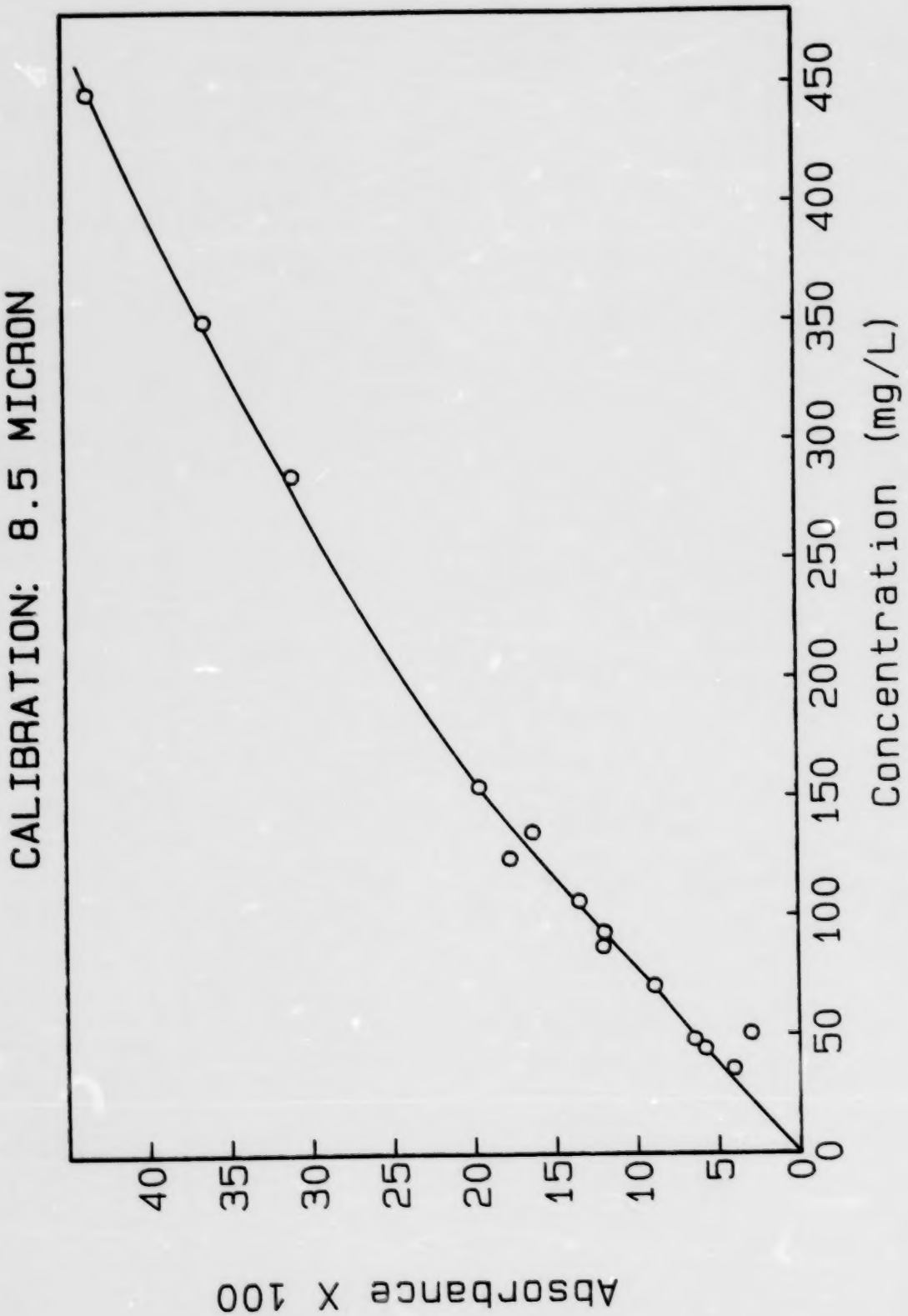
CALIBRATION: 8.5 MICRON
Absorbance X 100
0
5
10
15
20
25
30
35
40
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)

Fig.8.

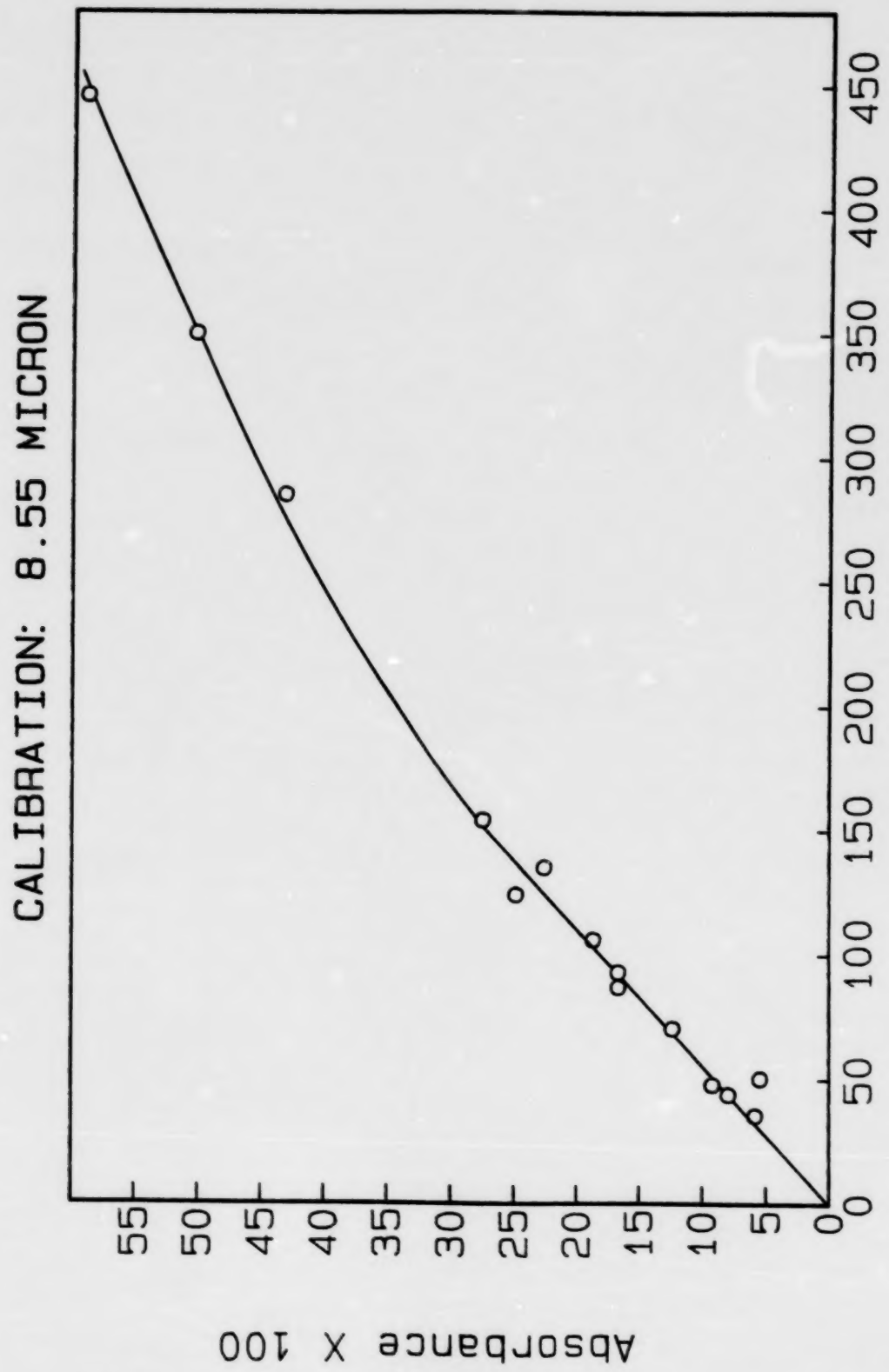
CALIBRATION: 8.55 MICRON
Absorbance X 100
Concentration (mg/L)
0
5
10
15
20
25
30
35
40
45
50
55
0
50
100
150
200
250
300
350
400
450

Fig. 9.

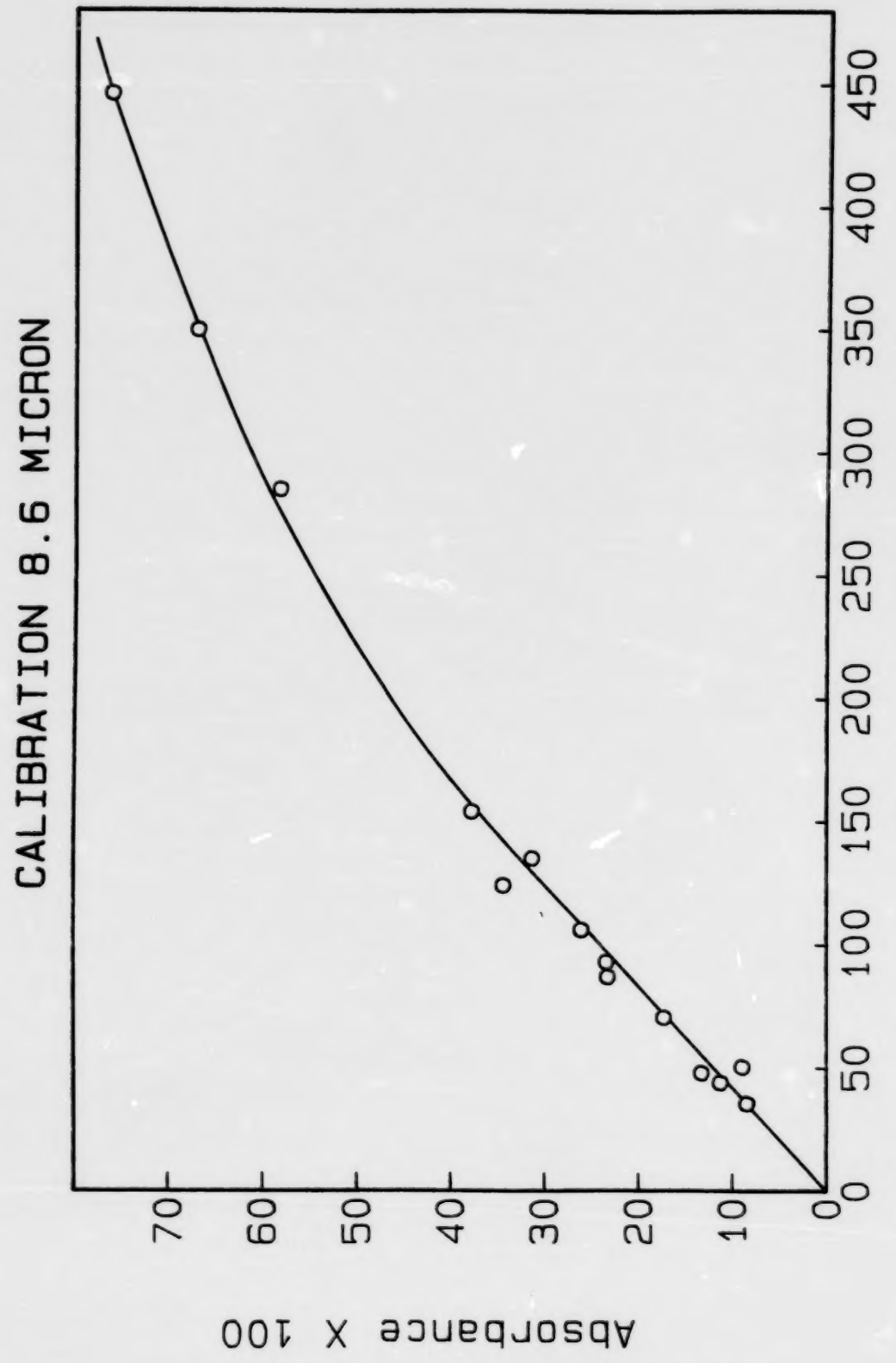
CALIBRATION 8.6 MICRON
Absorbance X 100
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)

Fig. 10

CALIBRATION 8.7 MICRON
Absorbance X 100
Concentration (mg/L)
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450

Fig. 11

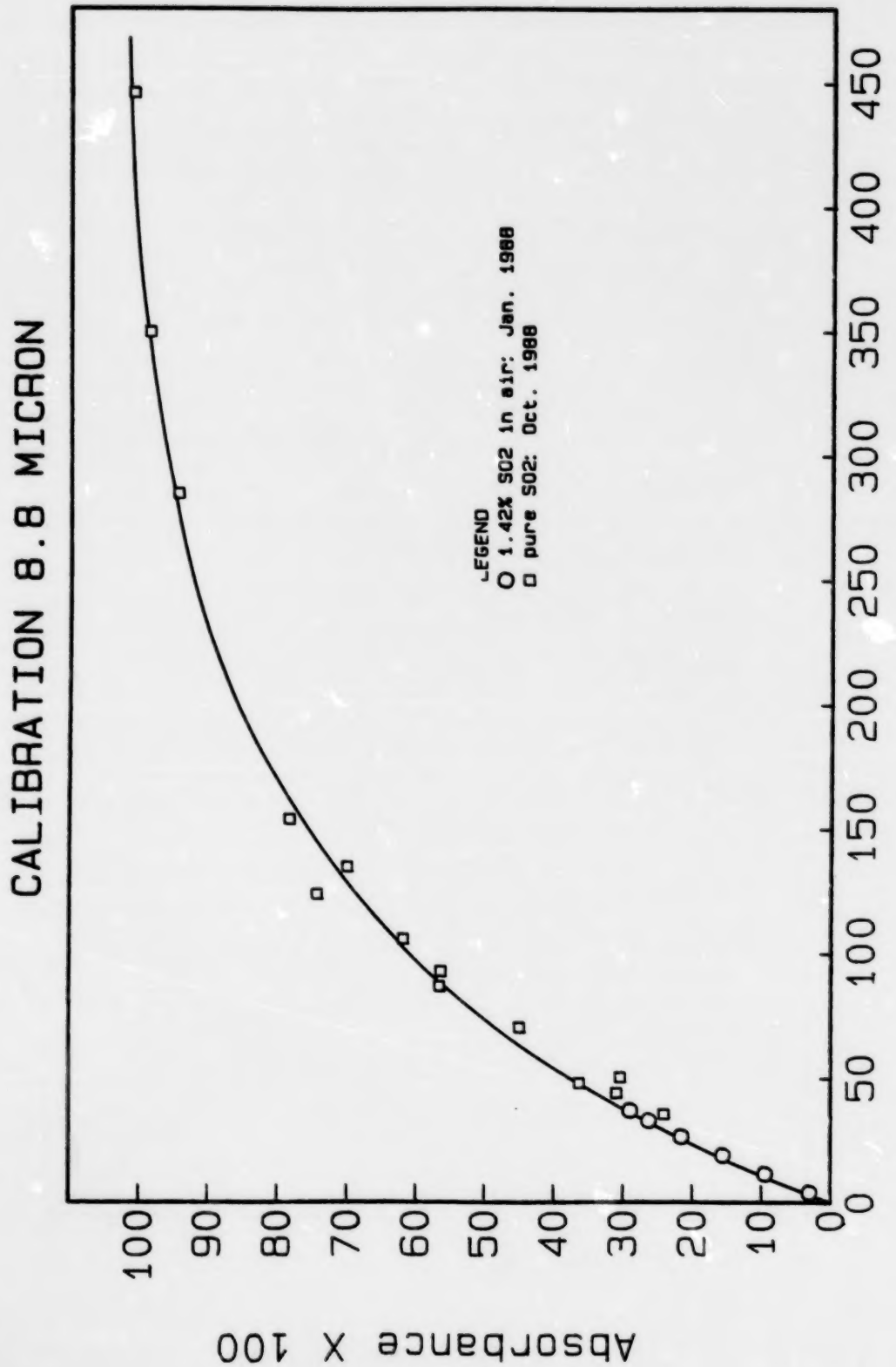
CALIBRATION 8.8 MICRON
LEGEND
O 1.42% SO2 in air: Jan. 1988
□ pure SO2: Oct. 1988
Absorbance X 100
Concentration (mg/L)
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450

Fig. 12

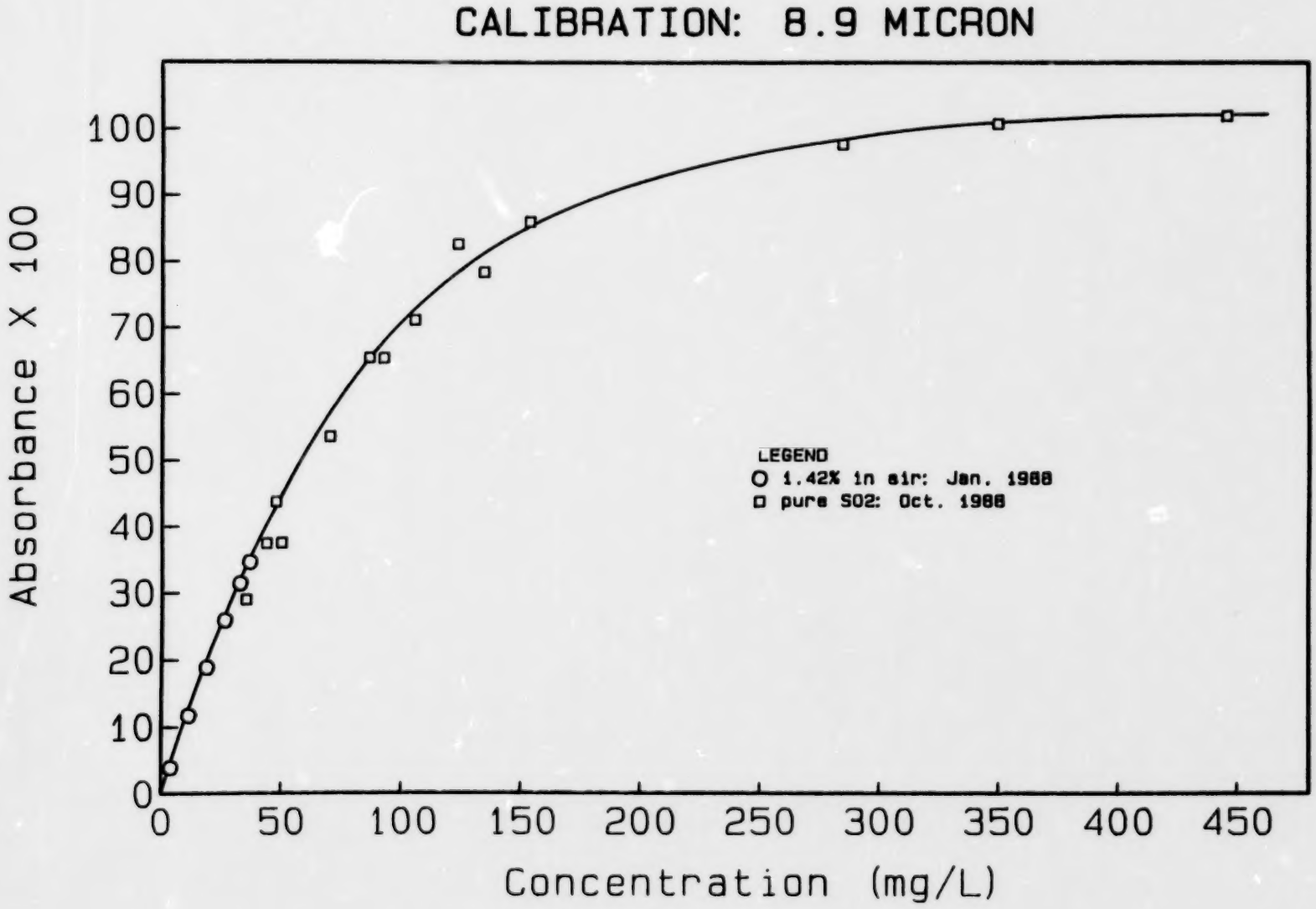
CALIBRATION: 8.9 MICRON
Absorbance X 100
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)
LEGEND
1.42% in air: Jan. 1988
pure SO2: Oct. 1988

Fig. 13

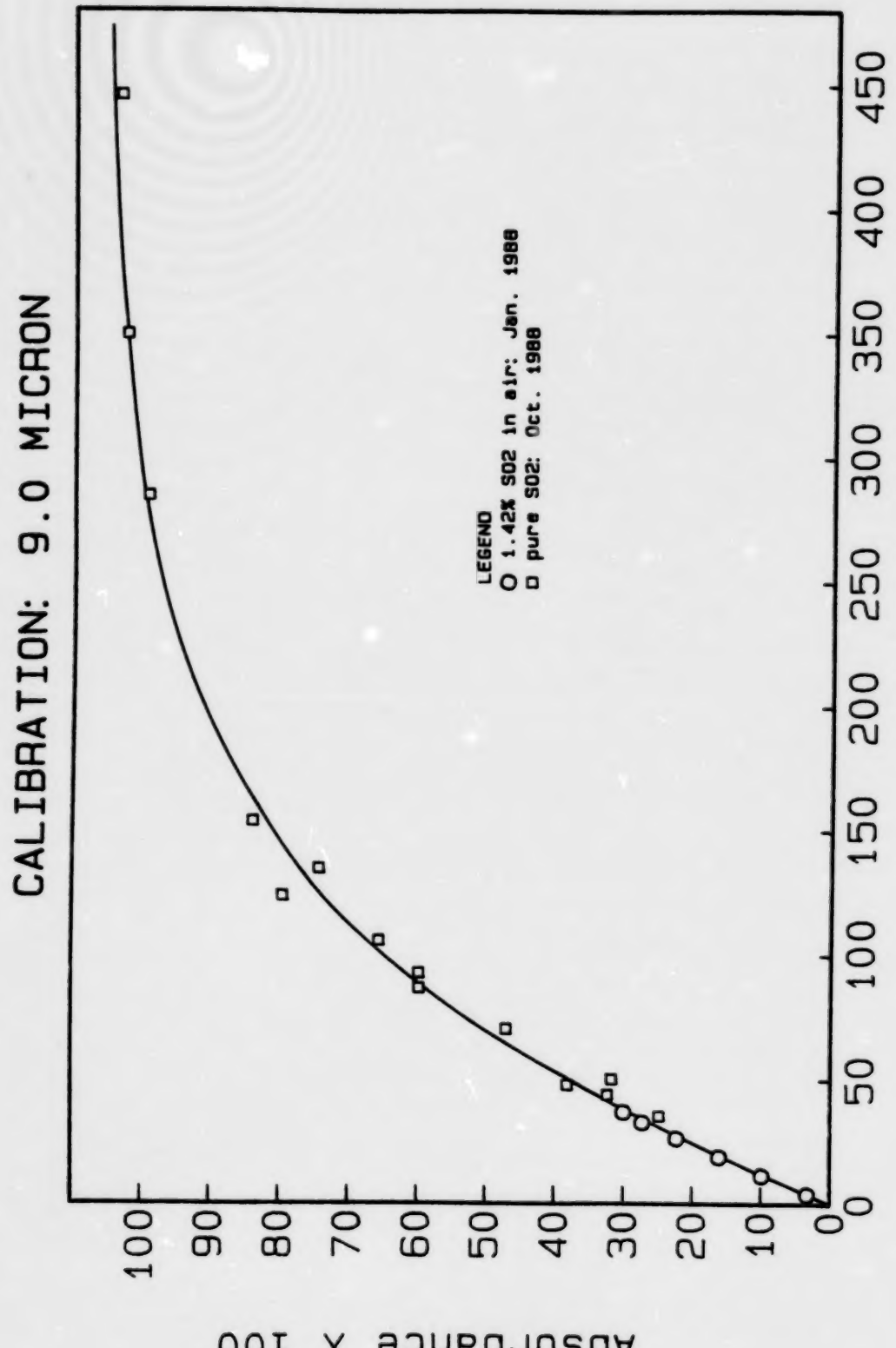
CALIBRATION: 9.0 MICRON
LEGEND
O 1.42% SO2 in air: Jan. 1988
□ pure SO2: Oct. 1988
Absorbance X 100
Concentration (mg/L)
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
450

Fig. 14

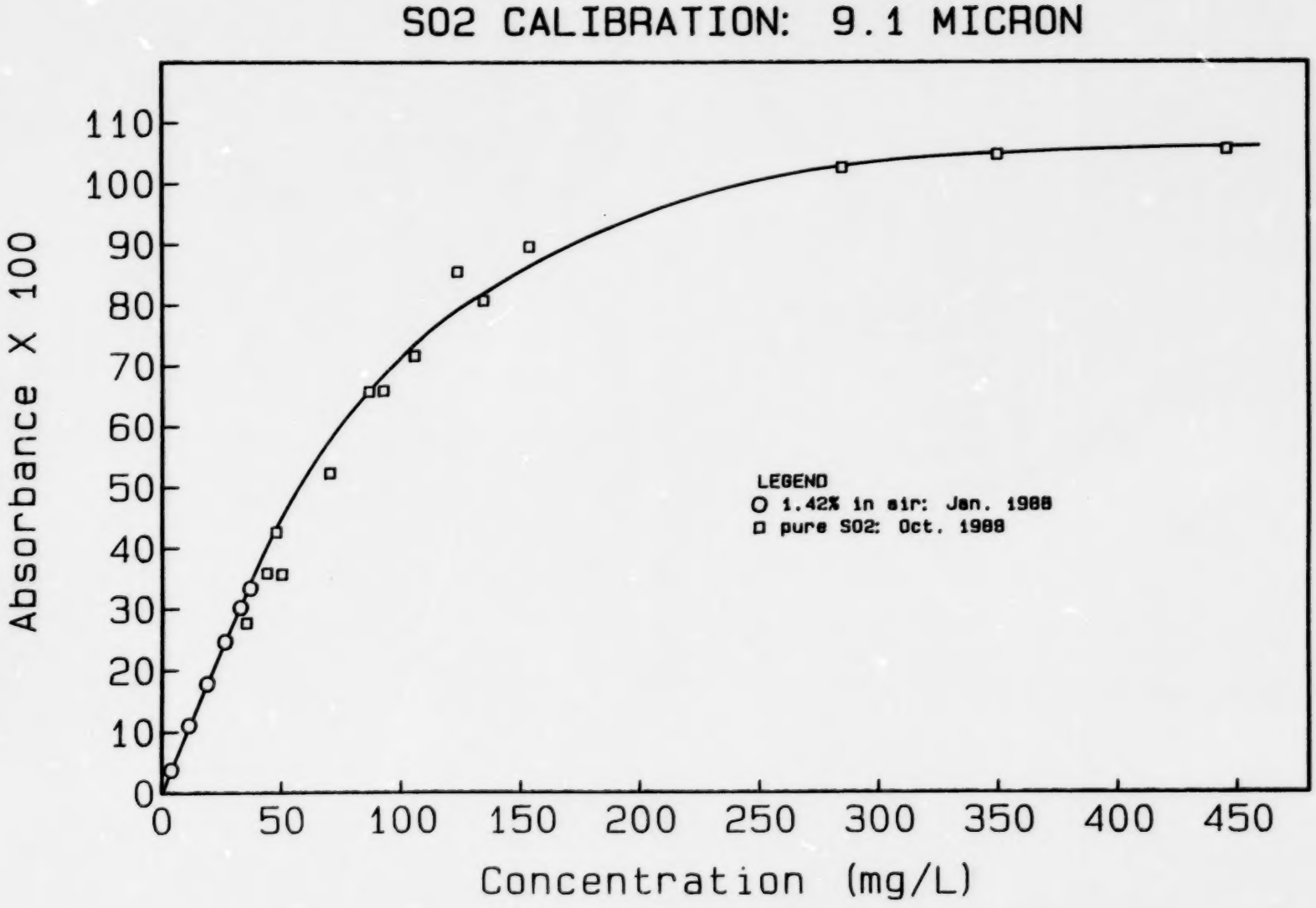
SO2 CALIBRATION: 9.1 MICRON
Absorbance X 100
0
10
20
30
40
50
60
70
80
90
100
110
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)
LEGEND
O 1.42% in air: Jan. 1988
□ pure SO2: Oct. 1988

Fig. 15

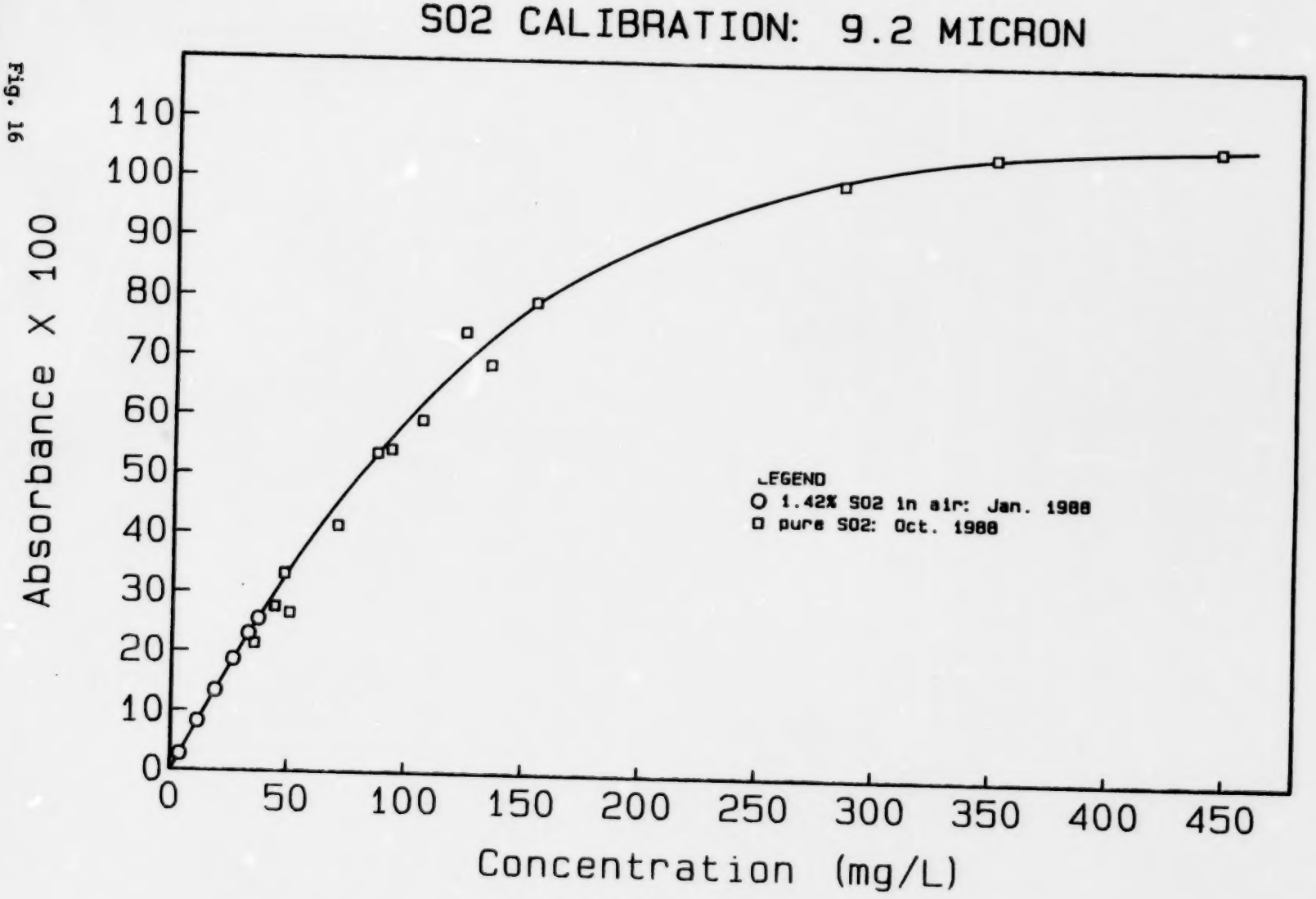
SO2 CALIBRATION: 9.2 MICRON
Absorbance X 100
Concentration (mg/L)
0
10
20
30
40
50
60
70
80
90
100
110
0
50
100
150
200
250
300
350
400
450
LEGEND
O 1.42% SO2 in air: Jan. 1988
□ pure SO2: Oct. 1988

Fig. 16

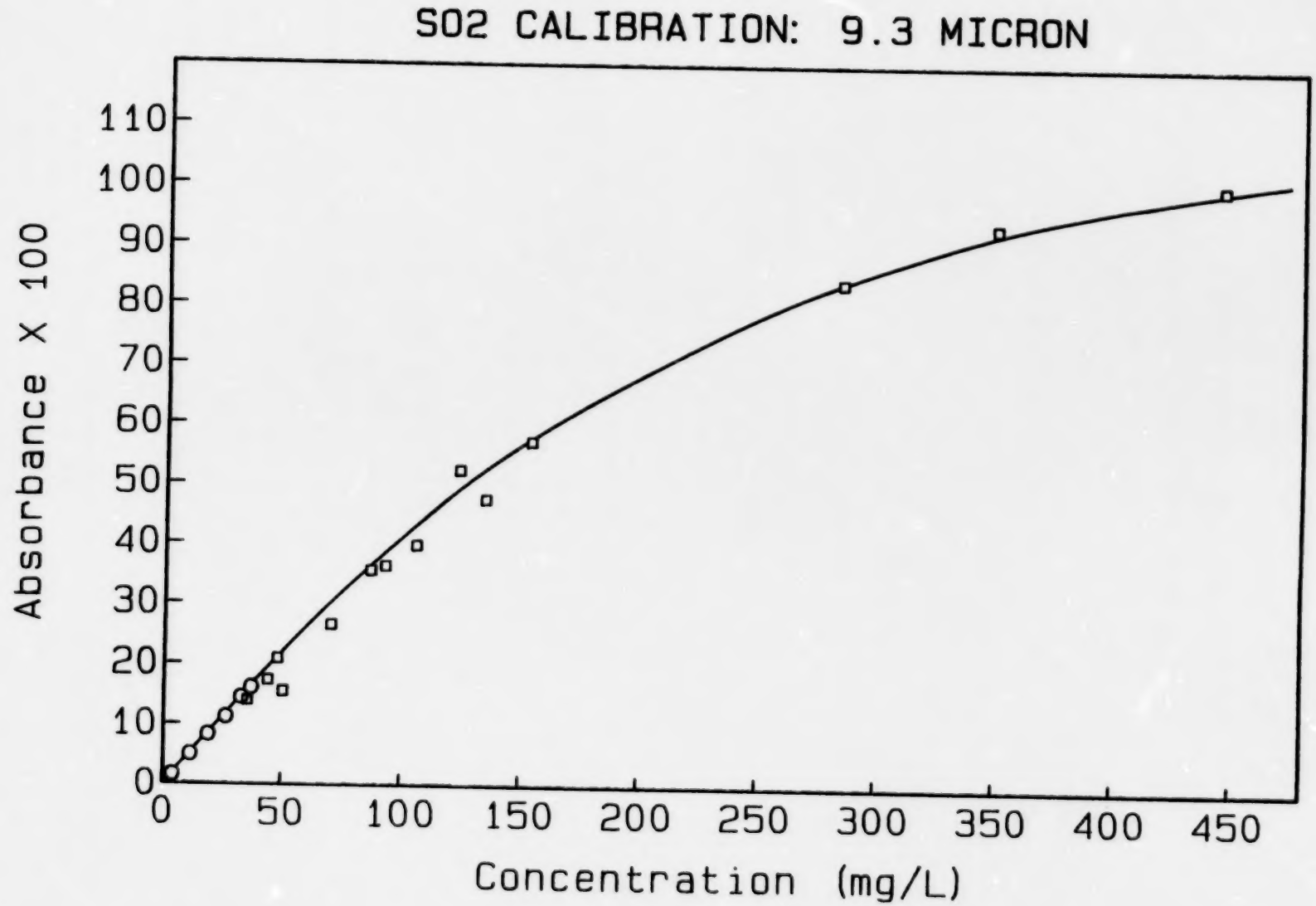
SO2 CALIBRATION: 9.3 MICRON
Absorbance X 100
0
10
20
30
40
50
60
70
80
90
100
110
0
50
100
150
200
250
300
350
400
450
Concentration (mg/L)

Fig. 17

APPENDIX

PROCEDURE FOR MEASURING SO_2 USING THE MIRAN-80 COMPUTING INFRARED ANALYZER

Preparation

1. Turn on the power for the MIRAN-80. (Normally, it should be left on, even when not in use.) If "MEMORY" light is not on, press 8531616, blue, blue. Wait at least one hour before proceeding with step 3.
2. Evacuate gas cell for at least one hour.
3. Check that the "MICRONS" light is on. If "WAVENUMBER" light is on instead, press "CLEAR", yellow, "W".
4. Press "CLEAR", "YELLOW", "PRT PARA". The printer will print out 6 lines.
   (a) "DCPS" should be 0. If not, press "clear", "blue", "A".
   (b) "NW" should be 13. If not, press "clear", 13, "blue", 2.
   (c) "NC" should be 0. If not, press "clear", 0, "blue", 3.
   (d) "SCSD" and "DLTM" can have any values.
   (e) "RDTM" should be 1. If not, press "clear", 1, "blue", 0.
5. Press "CLEAR", "yellow", "PRT W". The list of 13 wavelengths should be printed: 3.8, 8.4, 8.45, 8.5, 8.55, 8.6, 8.7, 8.8, 8.9, 9.0, 9.1, 9.2, 9.3; respectively, the reference wavelength, the first anaytical wavelength, the second analytical wavelength, etc.
6. If not, press "CLEAR", 1, "blue", 4, 3.8, "blue", 5, 8.4, "blue", 5, 8.45, "blue", 5, 8.5, "blue", 5, ...(for all the other wavelengths). Then repeat step 5.
7. Fill gas cell with 1 atmosphere dry air.

8. Press "CLEAR", "yellow", "SET GAIN". The instrument will display each wavelength in turn and will turn on the "ZERO SET" light. After it has finished, the "READY" light will turn on.
9. Press "CLEAR", "ZERO". The instrument will display each wavelength in turn and will turn on the "ZERO SET" light. After it has finished, the "READY" light will turn on.
10. Press "CLEAR", "ANALYZE". The "ANALYZE" light will go on, each wavelength in turn will be displayed, and an absorbance value printed.
11. After the completion of the printout, press "CLEAR". The "ANALYZE" light will go off and the "READY" light will go on.
12. Evacuate the gas cell.

Analysis

1. After the explosion test, allow the 20-L vessel to cool to room temperature. Ensure that the gas cell and the lines leading to it are under vacuum.
2. Open the plug valve leading to the gas cell and allow the gases to equilibrate for a few minutes.
3. Close the valve on the cell that leads from the 20-L vessel and open the other valve until the pressure has reached atmospheric.
4. Press "CLEAR", "ANALYZE". The "ANALYZE" light will go on, each wavelength in turn will be displayed, and the absorbance value for that wavelength will be printed.
5. After the completion of the printout, press "CLEAR". The "ANALYZE" light will go off and the "READY" light will go on.
6. Calculate the concentration at each wavelength using the "slope"

values listed in Table 1, provided that the absorbance value is greater than 0.04 and less than the value listed in Table 1.

7. For the other wavelengths, use the graphs to determine the concentration, provided that the absorbance value is less than that shown in Table 2.
8. Calculate the mean and standard deviation. Multiply by 0.0264 to obtain the total weight (in grams) of SO_2 produced.
9. Evacuate the cell for at least 15 minutes before the next test.